

Radius of Gyration of Randomly Branched Molecules

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Abstract

The mathematical derivation of the mean square radius of gyration, $\langle s_x^2 \rangle$, of branched polymers is reinvestigated from a kinetic-equation-point of view. In particular we derive the corresponding quantity of the A-R-B_{f-1} model; the result showing that the mean square radius of gyration is precisely identical with that of the R-A_f model.

Key Words: Mean Radius of Gyration/ Kramers Theorem/ Kinetic Equation

It is well established that the mean square radius of gyration for randomly branched polymers scales as $\langle s_x^2 \rangle \propto x^{\frac{1}{2}}$. This formula was derived by Zim & Stockmayer in 1949 [1], Dobson & Gordon in 1964 [2], and Kajiwara in 1971 [3]. The derivations are, however, much complicated and require harder mathematics. For this reason the result does not appear to have fully permeated into the community. In this report, we derive the same formula, in a elementary fashion, from a somewhat different point of view with the help of kinetic equation concept.

1 Kramers Theorem

By the elementary mathematics, it is obvious that

$$\vec{r}_{ij} = \vec{r}_{Gj} - \vec{r}_{Gi} \quad (1)$$

$$r_{ij}^2 = r_{Gi}^2 + r_{Gj}^2 - 2\vec{r}_{Gi} \cdot \vec{r}_{Gj} \quad (2)$$

Summing over all pairs, we have

$$\sum_{i=1}^N \sum_{j=1}^N r_{ij}^2 = 2N \sum_{i=1}^N r_{Gi}^2 - 2 \sum_{i=1}^N \sum_{j=1}^N \vec{r}_{Gi} \cdot \vec{r}_{Gj} \quad (3)$$

By definition, $\sum_{i=1}^x \vec{r}_{Gi} = 0$ and $s_x^2 = \frac{1}{x} \sum_{i=1}^x r_{Gi}^2$. Hence, taking the statistical average of eq. (3), we have

$$\langle s_x^2 \rangle = \frac{1}{2x^2} \sum_{i=1}^x \sum_{j=1}^x \langle r_{ij}^2 \rangle = \frac{1}{x^2} \sum_{i < j}^x \langle r_{ij}^2 \rangle \quad (4)$$

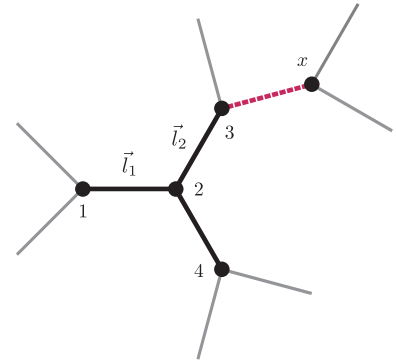


Fig. 1: A 3D vector field of an x -cluster.

This formula holds whether a molecule is linear or branched. For the random flight (Brownian) chain, we have $\langle r_{ij}^2 \rangle = l_i^2 + l_{i+1}^2 + \dots + l_{j-1}^2$. Now focus our attention on any one bond of those, for instance l_i . Then it is seen that the summation in eq. (4) simply represents the total number of trails that pass through the bond in question.

Let all bonds have an equal length, l . Cutting the k th bond should split the x -cluster into a k -cluster and an $(x-k)$ -cluster. Let us call these fragment clusters a $(k, x-k)$ pair. The above-mentioned number of trails is simply equal to $k \times (x-k)$. Let ω_k be a statistical weight to give a $(k, x-k)$ pair. There are $(x-1)\omega_k$ such $(k, x-k)$ pairs in the cluster. Thus we may recast eq. (4) in the form:

$$\langle s_x^2 \rangle = \frac{(x-1)}{x^2} l^2 \sum_{k=1}^{x-1} \omega_k k (x-k) \quad (5)$$

which is just the well-known Kramers theorem [4]. To find the mathematical form of ω_k , consider the equilibrium formation of an x -cluster, C_x , through the coupling reaction between the fragment molecules C_k and C_{x-k} :



What we are seeking is the quantity of randomly branched polymers. So we must proceed with our calculation making use of the quantity of molecules resulting from the equilibrium reaction.

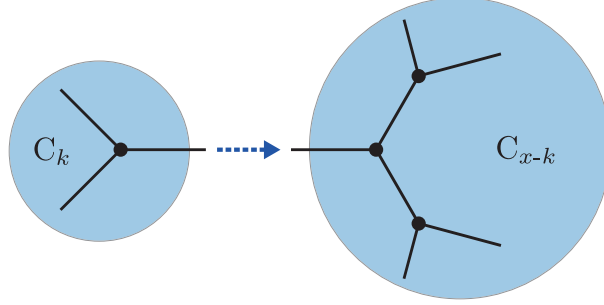


Fig. 2: A coupling reaction between fragment molecules.

2 R-A_f Model

It has been known [5,6] that the population of the k -cluster formed by eq. (c-1) is

$$N_k = M_0 \frac{f\{(f-1)k\}!}{k! \nu_k!} p^{k-1} (1-p)^{\nu_k} \quad (6)$$

where $M_0 = \sum_{k=1}^{\infty} k N_k$ denotes the total number of monomer units and $\nu_k = (f-2)k + 2$ the number of unreacted functional units on the k -cluster. It is clear that there are $\nu_k \nu_{x-k}$ chances for the formation of the k th bond on an x -cluster, whereas only one chance exists for the backward (dissociation) reaction. We may drop this latter factor, since it has no effect on our final result. Hence

$$\omega_k = \frac{\nu_k N_k \cdot \nu_{x-k} N_{x-k}}{\sum_{k=1}^{x-1} \nu_k N_k \cdot \nu_{x-k} N_{x-k}} \quad (7)$$

According to the mathematical theorem, the denominator reduces to

$$\sum_{k=1}^{x-1} \frac{\{(f-1)k\}!}{k! (\nu_k - 1)!} \cdot \frac{\{(f-1)(x-k)\}!}{(x-k)! (\nu_{x-k} - 1)!} = 2(x-1) \frac{\{(f-1)x\}!}{x! \nu_x!} \quad (8)$$

Hence

$$\omega_k = \frac{x}{2} \left\{ \frac{\frac{1}{k(x-k)} \binom{(f-1)k}{k-1} \binom{(f-1)(x-k)}{x-k-1}}{\binom{(f-1)x}{x-2}} \right\} \quad (9)$$

Substituting eq. (9) into eq. (5), we have

$$\langle s_x^2 \rangle = \frac{(x-1)l^2}{2x} \frac{\sum_{k=1}^{x-1} \binom{(f-1)k}{k-1} \binom{(f-1)(x-k)}{x-k-1}}{\binom{(f-1)x}{x-2}} \quad (10)$$

which may be recast in the alternative form [2]:

$$\langle s_x^2 \rangle = \frac{l^2}{2x^2} \frac{x! \{(f-2)x+2\}!}{\{(f-1)x\}!} \sum_{k=1}^{x-1} \binom{(f-1)k}{k-1} \binom{(f-1)(x-k)}{x-k-1} \quad (11)$$

3 A–R–B_{f-1} Model

In this case, we use the number distribution [6]:

$$N_k = M_0 \{1 - (f-1)p\} \frac{\{(f-1)k\}!}{k! \nu_k!} p^{k-1} (1-p)^{\nu_k} \quad (12)$$

where $\nu_k = (f-2)k+1$ is the number of unreacted functional units on a k -cluster. In this model, only A–B type bonds are possible, so that there are $\nu_k \times 1 + \nu_{x-k} \times 1 = \{(f-2)x+2\}$ chances for the k th bond formation, while a single chance exists for the dissociation reaction. Hence, dropping the constant term $\{(f-2)x+2\}$, we have

$$\omega_k = \frac{N_k \cdot N_{x-k}}{\sum_{k=1}^{x-1} N_k \cdot N_{x-k}} \quad (13)$$

which, with the help of the formula (8), again leads us to the expression:

$$\omega_k = \frac{x}{2} \left\{ \frac{\frac{1}{k(x-k)} \binom{(f-1)k}{k-1} \binom{(f-1)(x-k)}{x-k-1}}{\binom{(f-1)x}{x-2}} \right\} \quad (9')$$

Substituting into eq. (5), we obtain

$$\langle s_x^2 \rangle = \frac{l^2}{2x^2} \frac{x! \{(f-2)x+2\}!}{\{(f-1)x\}!} \sum_{k=1}^{x-1} \binom{(f-1)k}{k-1} \binom{(f-1)(x-k)}{x-k-1} \quad (11')$$

which is exactly the same result as the foregoing solution (11) for the R–A_f model. The result is unexpected, if we recall the fact that the two systems have entirely different gelation behavior [6].

4 Asymptotic Form of $\langle s_x^2 \rangle$ for a Large x

The Stirling formula is

$$x! \simeq \sqrt{2\pi x} (x/e)^x \quad (14)$$

for a large x . Let $g = f-1$ and $h = f-2$ [2]. Applying eq. (14) to eq. (11), and approximating the sum by the integral, we have

$$\begin{aligned} \langle s_x^2 \rangle &\simeq \frac{l^2 \{hx+1\} \{hx+2\}}{2x^2} \sqrt{\frac{gx}{2\pi h}} \int_1^{x-1} \frac{\sqrt{k(x-k)}}{\{hk+1\} \{h(x-k)+1\}} dk \\ &= \frac{l^2 \{hx+1\} \{hx+2\}}{2x^{3/2}} \sqrt{\frac{g}{2\pi h}} \left[\frac{2}{h^2} \left\{ \arctan \sqrt{\frac{k}{x-k}} \right. \right. \\ &\quad \left. \left. - \frac{\sqrt{hx+1}}{hx+2} \left(\arctan \sqrt{\frac{k(1+hx)}{x-k}} + \arctan \sqrt{\frac{k}{(x-k)(1+hx)}} \right) \right\} \right]_1^{x-1} \quad (15) \end{aligned}$$

As $x \rightarrow \infty$, since $0 \leq |\arctan z| \leq \pi/2$ by definition and $\arctan(\infty) = \pi/2$, the above equation reduces to

$$\langle s_x^2 \rangle \simeq \left(\frac{(f-1)\pi}{2^3(f-2)} \right)^{1/2} x^{\frac{1}{2}} l^2 \quad (16)$$

For a large x , the mean square radius of gyration of branched molecules increases as $\langle s_x^2 \rangle \propto x^{1/2}$, in contrast to that of linear molecules, $\langle s_x^2 \rangle \propto x$.

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